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From: Timothy M. Sivavec

SUBJECT: **PATENT DISCLOSURE LETTER**
           Remote Monitoring System for Permeable Reactive Barriers

1. OBJECT OF INVENTION

The invention relates to a remote monitoring, diagnostic, and reporting method and system that is designed to monitor the performance of permeable reactive barriers (PRBs). One of the most promising groundwater restoration technologies developed over the last few years has been the use of permeable reactive barriers filled with reactive materials to intercept and destroy contaminant plumes in the subsurface (1-14). Reactive material such as recycled cast iron (zero-valent iron) is placed into the subsurface to intercept a plume of contaminated groundwater which passes through the reactive material under its natural gradient, thereby creating a passive treatment system. As the contaminant passes through the granular iron material, the contaminants are adsorbed to the iron and are reduced to nontoxic end products. A wide variety of chlorinated hydrocarbons, including chlorinated ethenes such as trichloroethene (TCE) and tetrachloroethene (PCE), are effectively treated by this method, often at a significant cost savings when compared to conventional pump-and-treat alternatives. A significant number of toxic metals are also effectively treated using PRB technology (15).

Compliance monitoring of PRBs typically involves the monitoring of contaminants of interest at locations where dissolved concentrations have been detected and exceed regulatory limits. General water quality monitoring is also often included, such as the measurement of major cations and anions, alkalinity, and other water quality indicator parameters such as pH, dissolved oxygen, specific conductance, and oxidation-reduction potential.

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Well placement and design are important to ensure adequate assessment of system performance. In addition to placing wells upgradient and downgradient of the PRB, wells are often also located to ensure that contaminated water is not flowing around, under, or over the barrier wall. The number of wells used will depend on the design and size of the PRB. Wells of 2 inch diameter or even smaller (*e.g.*, ¾ inch inner diameter) are usually appropriate for compliance monitoring purposes. Low-flow sampling methods are typically used for compliance sampling purposes (16). Low-flow refers to the velocity with which water is withdrawn with a pump from the aquifer and is usually from 0.1 to 0.5 L/min, depending on site-specific hydrogeologic conditions. The objective is to pump groundwater to the surface for measurement and sample collection in a manner that minimizes stress to the hydrogeologic system. However, the action of pumping groundwater to the surface for measurement in an in-line flow cell often introduces atmospheric gases into the sampled groundwater. This is next to impossible to control. The use of in-well field indicator probes as disclosed in this letter avoids this source of error, in that the measurement is made in the well water directly.

Monitoring within the PRB itself poses a number of unique challenges. Low-purge methods are often inappropriate because the withdrawal of large volumes of water may compromise PRB sampling objectives. Data is often sought to confirm degradation rates that were used to design the PRB or to assess changes in iron media reactivity. These rates and changes may need to be addressed over relatively small spatial intervals. To do this accurately, water from much smaller volumes of the aquifer and within the PRB must be withdrawn. This is where the use of passive or semi-passive sampling approaches can provide advantages over conventional low-purge sampling methods. Several researchers have shown that discrete-level sampling approaches may be used to provide no-purge samples representative of formation water (17-20). A number of automated and manual groundwater monitoring systems have been patented in recent years, most of them requiring the use of pumps to withdraw groundwater to the surface for sampling and/or monitoring (21-24). Several others use devices to monitor groundwater characteristic in general aquifer environments (24-25). This letter shows that such a monitoring system can be used to monitor the performance of a PRB under a geochemical environment quite different from that of an aquifer or landfill.

Water quality indicator parameters are often used to determine purging needs prior to sample collection in each well. Stabilization of parameters such as pH, specific conductance, dissolved oxygen, oxidation-reduction potential, temperature and turbidity is used to determine when formation water (as opposed to well or borehole water) is accessed during purging. Most of these same parameters are important performance indicators for PRBs composed of granular iron. Many of these parameters are important as indicators of the corrosion process for iron-mediated transformations within the iron PRB. For example, it is common to measure significantly reduced specific conductivities within the iron media relative to up- and downgradient monitoring points. Significantly higher pH values are also measured within the iron PRB relative to monitoring points elsewhere in the aquifer. PH values of between 9 and 11 are commonly observed, as compared to near neutral pH (ph 7) elsewhere in the aquifer. Similarly, oxidation-reduction values are significantly lower measured in a well location within an iron PRB as compared to up- or downgradient of the PRB.

This invention then addresses the need to measure important field indicator parameters (sometimes called groundwater quality parameters) using a passive technique that does not require the retrieval of formation water by use of a pump. This method provides a method to gain such data in near, real-time and to access such data remotely.

2. DESCRIPTION OF INVENTION

The invention provides a remote monitoring, diagnostics, and reporting system and method for monitoring the performance of a permeable reactive barrier (PRB). The invention provides real-time and historic data and increased data density relative to conventional low-flow sampling of formation water to improve understanding of processes occurring in and around PRBs. The monitoring system can be used to determine groundwater characteristics such as pH, dissolved oxygen, specific conductance, and oxidation-reduction potential. These field indicator parameters are particularly useful in assessing the performance of an iron PRB, as they are much changed in the presence of zero-valent iron owing to the corrosion reaction between iron and water under reducing conditions.

For example, within a 100% iron PRB, pH is typically increased from neutral to a value between 9 and 11. Dissolved oxygen will also be reduced in the presence of zero-valent iron. As most PRBs are emplaced in anaerobic aquifers where no significant dissolved oxygen is found, this is not usually very important in evaluating performance of a PRB. However, if water is being treated above-ground, dissolved oxygen is commonly introduced into the pumped groundwater and can result in clogging or cementation of the iron at the entrance to the iron system. Hence, monitoring for dissolved oxygen in above-ground applications can be useful in sustaining performance over the long term. Specific conductance of a groundwater sample is often reduced significantly (e.g., by 50% or more) in the presence of 100% iron. Oxidation-reduction potential is also a direct measure of the reducing environment of the iron media. It often measure less than –400 mV.

The monitoring system comprises an in-well module containing at least one sensor. The module may include any number of sensor that may be used to monitor groundwater characteristics. The module is placed down a groundwater well, typically at the mid-point of the screened interval. Groundwater wells include, but are not limited to, private and municipal drinking water wells, pollution control wells, and landfill monitoring wells. The wells can be spread throughout a remediation site to also provide data on groundwater elevation and gradients. The module includes a communications unit, which is electronically coupled to the module and is capable of transmitting data to a data collection center. The signals may be communicated, for example, from a well transceiver to the data collection system by at least one hardwired communication connection, such as, but not limited to, an electrical conductor, wireless communication connections, such as, but not limited to, radio signals, satellite communications and combinations of wireless and hardwired connections. The communications unit also typically comprises an antenna that is connected to the transceiver, unless the communications unit is hardwired.

The data collection center comprises a center communications unit that is capable of receiving signals from the transceiver and a control that analyzes the signals and generates information on groundwater characteristics. The control of the data collection system typically includes a "user friendly" data acquisition software package that transforms information into easy-to-read formats.

The information transmitted to the data collection center contains data representative of groundwater characteristics important to monitoring PRB performance. The report format provides real-time information and historical trend analysis of groundwater within and around a PRB installation. The real-time information permits a quicker response to undesirable groundwater characteristics, such as a rise in groundwater elevation caused by changes in the hydraulic conductivity of the PRB. It also provides trend analysis of oxidation-reduction potential, pH, specific conductivity, all indicative of an active corrosion environment within an iron PRB.

The monitoring system typically reduces monitoring and reporting costs at a PRB remediation site and provides enhances, readily available data more frequently than conventional monitoring systems that require one or more operators actively purging a number of wells at a given site. It also removes an important source of error in oxidation-reduction potential and dissolved oxygen measurements. That source of error is the introduction of atmospheric gases into the withdrawn groundwater leading to inaccurate measurements. The magnitude of such effects is shown in the reduction to practice data, where the low-flow purge method is compared directly with the in-well monitoring system at the same wells over an extended period.

3. REDUCTION TO PRACTICE

The invention has been fully reduced to practice in the field at Somersworth Sanitary Landfill Superfund Site, Somersworth, NH. An extended field test was performed evaluating the long-term performance of a constructability PRB test cell containing 100% granular iron. Four well modules were deployed in 4 well location, one upgradient of the iron zone, two within the iron zone, and one downgradient of the iron zone (see attached Figure). The four well location were along a transect in the direction of groundwater flow at the site. Table 1 compares temperature, pH, specific conductivity, dissolved oxygen, and oxidation-reduction potential measured by the in-well monitoring system and the conventional low-flow purge method. The high dissolved (DO) values and the more positive oxidation-reduction potential (ORP) values measured by the low-flow purge method are clearly in error, as a groundwater cannot be highly reducing (<-100 mv ORP) and contain such high concentrations of dissolved oxygen (~3.5 mg/L). This type of data is not uncommon when low-flow purge methods are used.

4. RECORDS

This invention and its reduction to practice are disclosed in Notebook C-243 assigned to T.M. Sivavec.

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DRAFT

CT-6

CT-4
CTC-C
CT-5
CT-2
CT-3
CTC-B

CTC-D

CTC-A

CT-1

Inferred direction of
groundwater flow
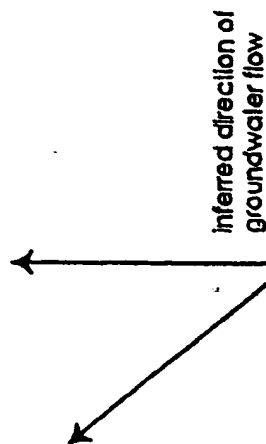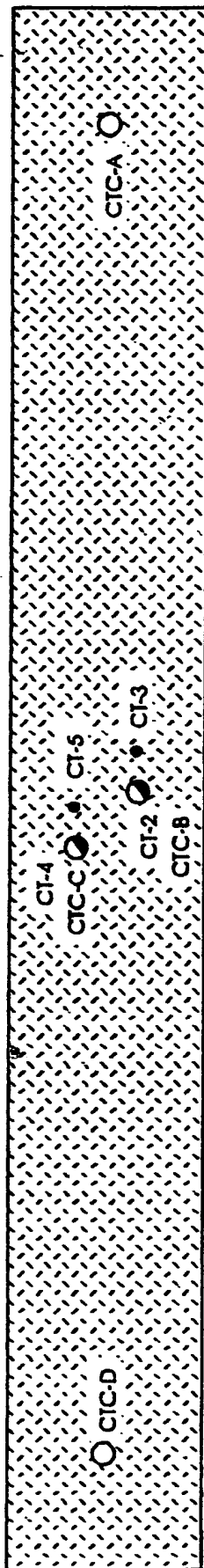
•   3/4" monitoring well

◑   core sample location and 2' monitoring well

●   2" monitoring well

○   core sample location

▨   chemical treatment wall test section

Locations of Core Samples and Monitoring Wells
for the Bioslurry Constructability Test
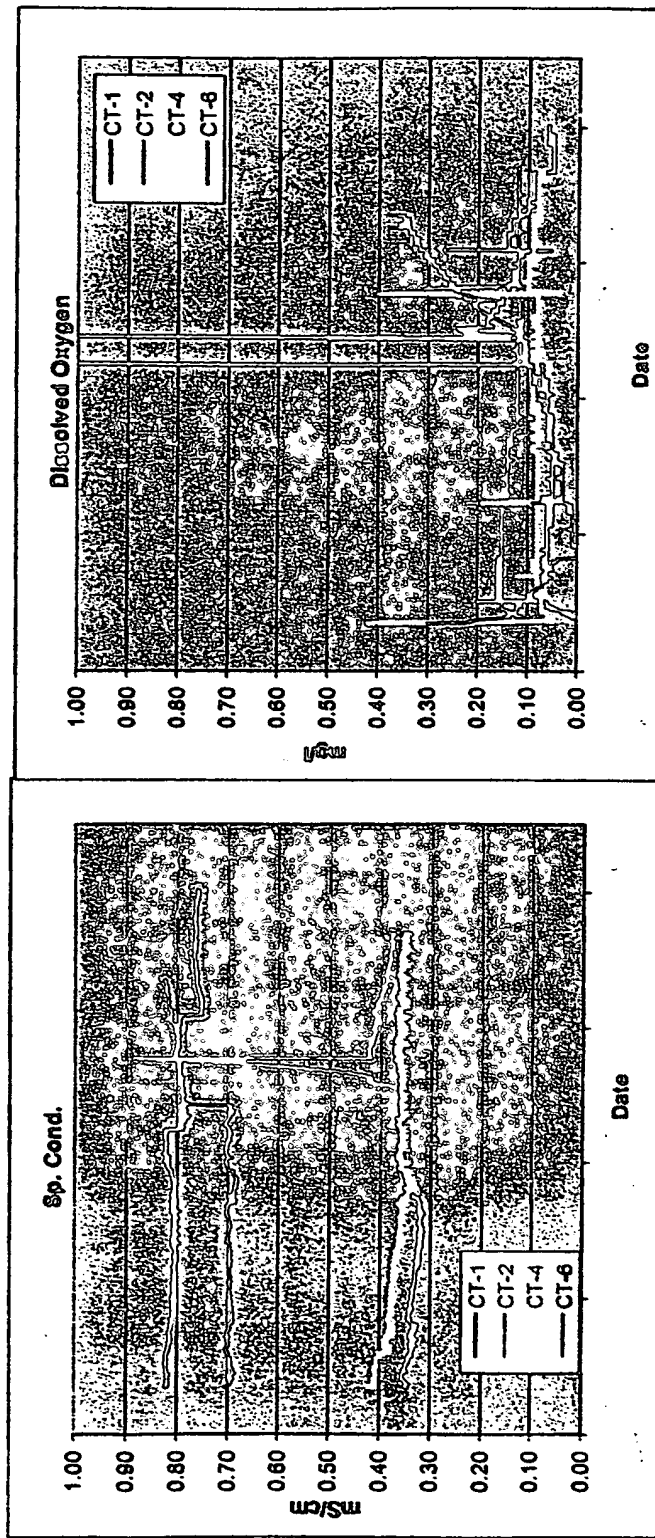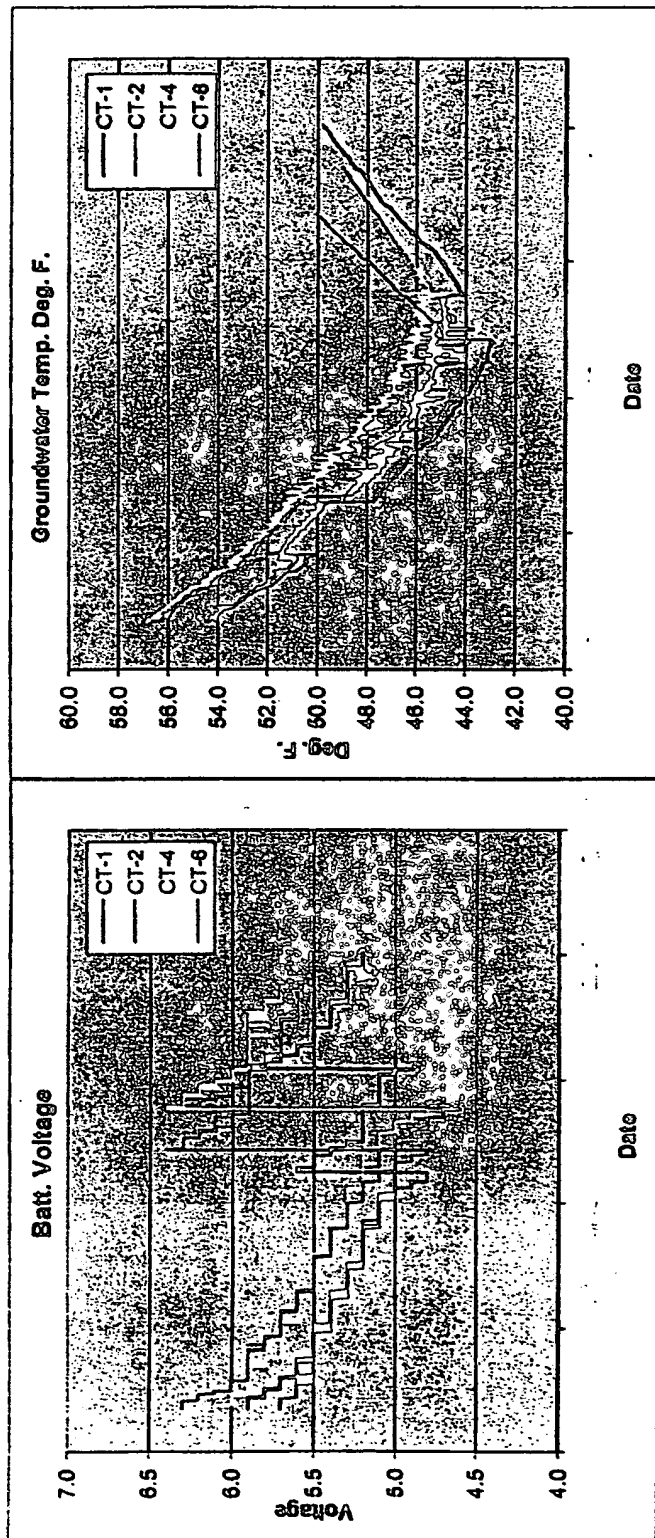Somersworth Landfill Superfund Site, Somersworth, NH

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Figure: 3

FIELD DATA COMPARISON FROM SOMERSWORTH NH SITE

LOOKING AT LOW-PURGE DATA COMPARED TO INSITU DATA

WELL	DATE	Method	TEMP Deg. C.	pH s.u.	SpCond uS/cm	DO mg/l	ORP mV
CT-1		Purge	11.35	6.21	810	3.54	-121
	@13:30	Insitu	11.94	6.57	816	0.05	-71
		Purge	9.40	6.46	793	0.79	-145
	@10:55	Insitu	11.10	6.59	811	0.06	-90
		Purge	9.30	6.40	821	3.50	-160
	@10:30	Insitu	10.47	6.61	806	0.06	-93
CT-6		Purge	11.05	6.31	837	1.55	-147
	@14:00	Insitu	12.13	6.69	685	0.12	-413
		Purge	8.73	6.56	820	0.65	-205
	@09:40	Insitu	10.89	6.70	692	0.03	-392
		Purge	8.40	6.50	851	2.50	-185
	@10:45	Insitu	8.59	6.70	694	0.04	-369
CT-3		Purge	10.90	8.50	461	0.65	-578
CT-2	@10:00	Insitu	13.19	9.71	356	0.15	-744
CT-3		Purge	8.78	8.57	504	0.78	-441
CT-2	@13:00	Insitu	11.45	9.83	343	0.15	-737
CT-3		Purge	9.60	9.00	524	3.30	-457
CT-2	@12:30	Insitu	10.29	9.93	330	0.14	-710
CT-5		Purge	10.89	9.18	427	0.45	-676
CT-4	@11:00	Insitu	13.36	9.70	409	0.06	-752
CT-5		Purge	7.24	9.73	438	0.71	-410
CT-4	@13:40	Insitu	11.69	9.90	382	0.08	-696
CT-5		Purge	9.60	9.70	469	2.60	-522
CT-4	@12:50	Insitu	10.47	10.10	373	0.08	-739

IN SITU PROBE DATA
Somersworth Sanitary Landfill Superfund Site, NH

Groundwater Temp. Deg. F.

Deg. F.

| CT-1 |
| CT-2 |
| CT-4 |
| CT-8 |

60.0
58.0
56.0
54.0
52.0
50.0
48.0
46.0
44.0
42.0
40.0

Date

Dissolved Oxygen

mg/l

| CT-1 |
| CT-2 |
| CT-4 |
| CT-8 |

1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00

Date

Batt. Voltage

Voltage

| CT-1 |
| CT-2 |
| CT-4 |
| CT-8 |

7.0
6.5
6.0
5.5
5.0
4.5
4.0

Date

Sp. Cond.

mS/cm

| CT-1 |
| CT-2 |
| CT-4 |
| CT-8 |

1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00

Date

Somersworth YSI Data

IN SITU PROBE DATA
Somersworth Sanitary Landfill Superfund Site, NH

Redox

Groundwater Level amsl

pH

Total Dissolved Solids

Somersworth YSI Data
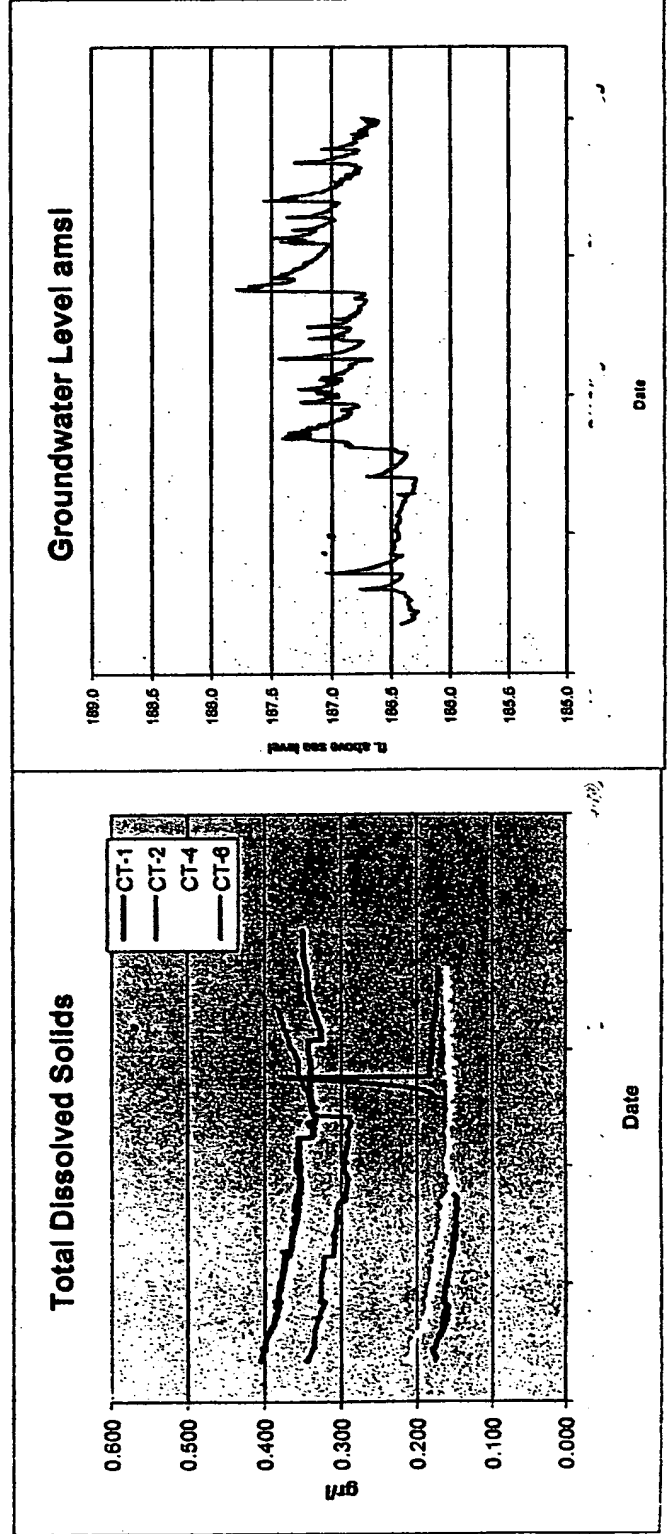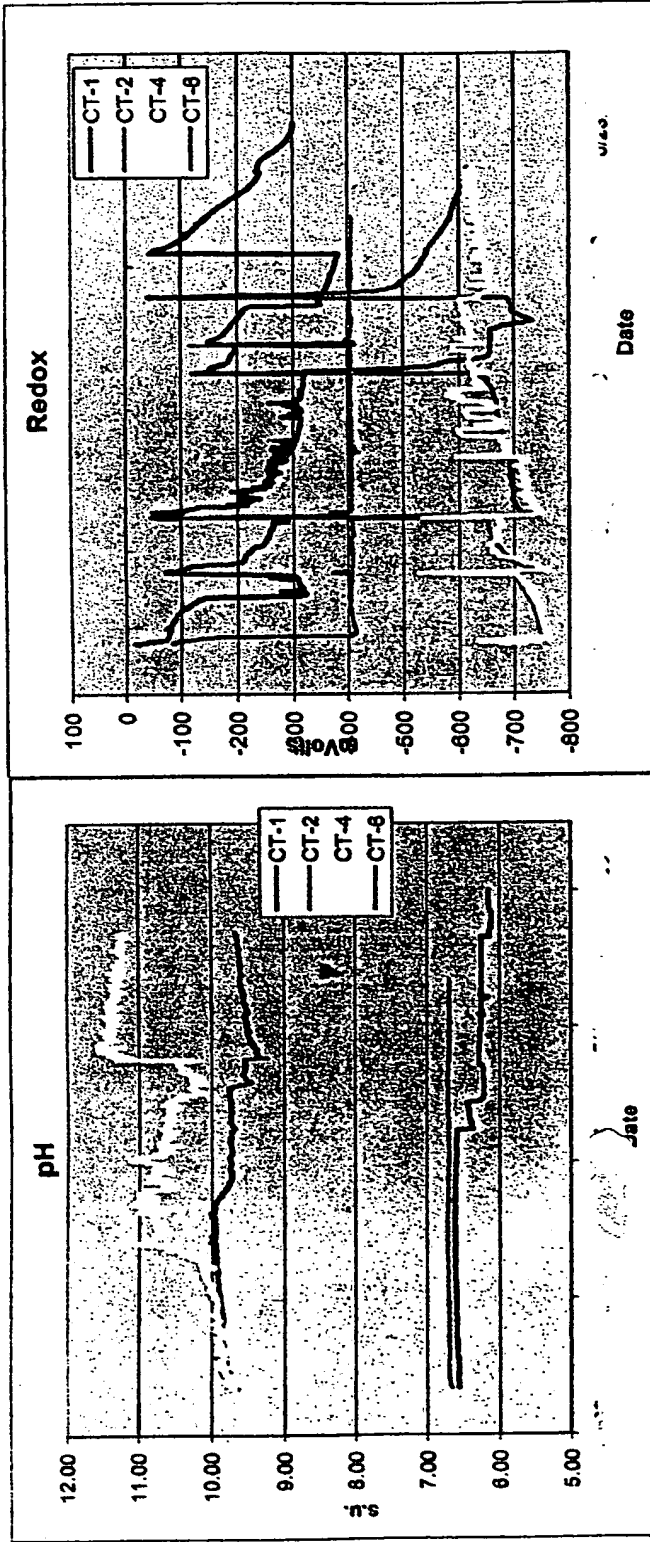
Summary Sheet of Sonde data

CT-1

Date time MDY		Battery V	Temp F	Depth ft	Depth Corrected	Spec Cond mS/cm	DO Conc mg/L	DO %	pH std	ORP mV	TDS g/L
	Average	5.7	52.48	15.013	186.623	0.817	0.05	0.5	6.58	-159	0.393
	max	5.9	54.45	15.607	187.217	0.823	0.20	1.8	6.59	-15	0.406
	min	5.5	50.79	14.833	186.443	0.809	-0.05	-0.5	6.56	-324	0.381
	Average	5.4	50.64	16.610	188.220	0.807	0.06	0.5	6.60	-222	0.378
	max	5.5	51.99	16.689	188.299	0.811	0.07	0.6	6.61	-73	0.387
	min	5.4	49.61	14.976	186.586	0.804	0.05	0.5	6.59	-294	0.371
	Average	5.2	46.83	15.304	186.914	0.810	0.06	0.5	6.61	-268	0.358
	max	5.4	50.84	16.380	187.990	0.827	0.17	1.5	6.63	-45	0.378
	min	5.0	44.81	14.172	185.782	0.796	0.04	0.3	6.58	-321	0.352
	Average	5.2	44.71	15.450	187.060	0.794	0.15	1.2	6.29	-263	0.339
	max	5.6	45.52	16.180	187.790	0.802	0.24	1.9	6.44	-121	0.344
	min	5.0	43.68	15.098	186.708	0.777	0.11	0.9	6.21	-383	0.332
	Average	5.2	44.72	15.452	187.062	0.794	0.15	1.2	6.29	-264	0.339
	max	5.9	45.52	16.180	187.790	0.802	0.26	2.2	6.44	-43	0.344
	min	4.9	43.68	15.098	186.708	0.752	0.06	0.5	6.21	-383	0.325
Total Average		5.3	47.73	15.485	187.095	0.806	2.15	17.8	6.50	-241	0.361
max		5.9	54.45	16.689	188.299	0.827	30.72	254.1	6.63	-15	0.406
min		5.0	43.68	14.172	185.782	0.777	-0.05	-0.5	6.21	-383	0.332

CT-2

Date time MDY		Battery V	Temp F	Depth ft	Depth Corrected	Spec Cond mS/cm	DO Conc mg/L	DO %	pH std	ORP mV	TDS g/L
	Average	5.6	54.61	14.961	186.581	0.341	0.14	1.4	9.83	-732	0.169
	max	5.7	56.61	15.536	187.156	0.356	0.20	1.9	9.94	-701	0.180
	min	5.5	52.87	14.822	186.442	0.325	0.07	0.7	9.64	-752	0.157
	Average	5.4	51.73	14.923	186.543	0.336	0.15	1.4	9.89	-677	0.160
	max	5.5	52.68	14.989	186.609	0.344	0.15	1.4	9.93	-649	0.166
	min	5.4	50.68	14.871	186.491	0.326	0.15	1.3	9.83	-737	0.154
	Average	5.2	48.58	14.693	186.313	0.339	0.13	1.1	9.86	-678	0.154
	max	5.4	51.07	16.221	187.841	0.364	0.22	2.0	10.03	-403	0.161
	min	4.8	46.27	12.806	184.426	0.314	0.11	1.0	9.71	-716	0.144
	Average	4.9	45.15	15.646	187.266	0.430	0.12	1.0	9.66	-643	0.185
	max	5.2	45.95	16.350	187.970	0.881	0.13	1.1	9.77	-256	0.379
	min	4.6	44.40	15.285	186.905	0.357	0.11	0.9	9.44	-733	0.155
	Average	5.8	45.81	15.267	186.887	0.404	0.12	1.0	9.69	-644	0.175
	max	6.3	47.69	16.350	187.970	0.881	0.27	2.2	9.77	-40	0.379
	min	5.6	44.40	12.806	184.426	0.351	0.11	0.9	9.22	-733	0.155
Total Average		5.4	48.89	15.130	186.750	0.370	0.13	1.2	9.74	-644	0.168
max		6.3	56.61	16.350	187.970	0.881	0.31	2.6	10.03	-40	0.379
min		4.6	44.40	12.806	184.426	0.314	0.07	0.7	9.22	-752	0.144

CT-4

Date/Time M/D/Y		Battery V	Temp F	Depth ft	Depth Corrected	Sp.Cond mS/cm	DO Conc mg/L	DO %	pH	ORP 0.65 mV	Sal ppt
	Average	5.9	54.97	14.751	186.521	0.397	0.08	0.8	9.85	-733	0.198
	max	6.1	56.87	15.331	187.101	0.422	0.42	4.0	9.98	-631	0.216
	min	5.7	53.02	14.612	186.382	0.378	0.05	0.5	9.67	-759	0.184
	Average	5.7	52.02	14.680	186.450	0.377	0.08	0.7	9.99	-680	0.180
	max	5.7	53.11	14.745	186.515	0.384	0.08	0.8	10.13	-526	0.186
	min	5.6	50.96	14.632	186.402	0.370	0.08	0.7	9.87	-753	0.175
	Average	5.4	48.59	15.049	186.819	0.358	0.08	0.7	10.70	-672	0.163
	max	5.6	51.25	15.689	187.459	0.374	0.19	1.7	11.14	-532	0.176
	min	5.2	46.45	14.159	185.929	0.337	0.08	0.7	9.95	-748	0.152
	Average	5.1	45.94	15.232	187.002	0.360	0.08	0.7	10.43	-612	0.157
	max	5.2	46.71	16.067	187.837	0.367	0.09	0.7	10.71	-587	0.160
	min	4.8	44.69	15.030	186.800	0.353	0.08	0.7	10.09	-653	0.154
	Average	6.0	47.08	15.264	187.034	0.359	0.09	0.8	11.33	-622	0.159
	max	6.4	48.84	15.838	187.608	0.371	0.40	3.4	11.59	-331	0.165
	min	5.7	45.49	14.900	186.670	0.348	0.04	0.3	10.38	-661	0.152
Total Average		5.6	49.08	15.051	186.821	0.366	0.08	0.7	10.63	-659	0.168
max		6.4	56.87	16.067	187.837	0.422	0.42	4.0	11.59	-331	0.216
min		4.8	44.69	14.159	185.929	0.337	0.04	0.3	9.67	-759	0.152

CT-6

Date/Time M/D/Y		Battery V	Temp F	Depth ft	Depth Corrected	Sp.Cond mS/cm	DO Conc mg/L	DO %	pH	ORP 0.65 mV	Sal ppt
3/5	Average	6.0	52.26	14.579	186.459	0.696	0.09	0.9	6.69	-378	0.334
	max	6.3	54.31	15.167	187.047	0.705	0.30	2.8	6.71	-84	0.347
	min	5.8	50.39	14.401	186.281	0.685	0.04	0.4	6.66	-414	0.322
	Average	5.7	50.72	18.527	190.407	0.694	0.01	0.1	6.71	-407	0.325
	max	5.9	51.60	18.646	190.526	0.697	0.02	0.2	6.71	-372	0.329
	min	5.6	49.85	14.528	186.408	0.689	-0.06	-0.5	6.70	-411	0.320
	Average	5.4	45.34	14.897	186.777	0.695	0.06	0.5	6.71	-402	0.300
	max	5.6	47.79	15.580	187.460	0.704	0.10	0.8	6.73	-104	0.312
	min	5.1	43.33	13.862	185.742	0.682	0.03	0.2	6.69	-420	0.290
	Average	4.9	43.07	15.141	186.911	0.697	0.10	0.8	6.70	-404	0.290
	max	5.1	43.32	15.659	187.429	0.706	0.11	0.9	6.71	-403	0.294
	min	4.8	42.87	14.640	186.410	0.688	0.09	0.8	6.69	-405	0.286
	Average	5.9	47.35	15.066	186.836	0.804	0.26	2.2	6.70	-396	0.358
	max	6.4	50.04	16.232	188.002	0.824	0.50	4.1	6.72	-91	0.383
	min	5.7	44.56	13.422	185.192	0.786	0.10	0.8	6.67	-407	0.335
Total Average		5.7	47.64	15.386	187.226	0.729	0.12	1.0	6.70	-397	0.326
max		6.4	54.31	18.646	190.526	0.824	0.50	4.1	6.73	-84	0.383
min		4.8	42.87	13.422	185.192	0.682	-0.06	-0.5	6.66	-420	0.286

Survey Point	FS	BS	Elevation	DTW 2/12/	Elev
FS-11 PVC		4.99	192.47		Notes:
FS-13 PVC		5.29	192.14		PVC = top of PVC well casing
TW-1 PVC	5.8		191.65		TOC = top of protective (outer) casing
TW-1 TOC	5.26		192.19	6.12	186.1 GRND = ground elevation
TW-1 GRND	7.86		189.59		
TW-2 PVC	5.77		191.68		
TW-2 TOC	5.02		192.43	5.91	186.5
TW-2 GRND	7.77		189.68		
TW-3 PVC	5.94		191.51		
TW-3 TOC	5.03		192.42	5.90	186.5
TW-3 GRND	7.96		189.49		
TW-4 PVC	5.47		191.98		
TW-4 TOC	4.95		192.50	5.64	186.9
TW-4 GRND	7.66		189.79		
CT-1 PVC	3.34		194.11		
CT-1 TOC	2.86		194.59	8.21	186.4
CT-1 GRND	5.27		192.18		
CT-2 PVC	3.33		194.12		
CT-2 TOC	2.7		194.75	8.40	186.3
CT-2 GRND	5.23		192.22		
CT-3 PVC	4.18		193.27		
CT-3 TOC	3.56		193.89		
CT-3 GRND	5.31		192.14		
CT-4 PVC	3.18		194.27		
CT-4 TOC	2.68		194.77	8.43	186.3
CT-4 GRND	5.19		192.26		
CT-5 PVC	3.66		193.79		
CT-5 TOC	3.5		193.95		
CT-5 GRND	5.29		192.16		
CT-6 PVC	3.07		194.38		
CT-6 TOC	2.63		194.82	8.50	186.3
CT-6 GRND	5.15		192.30		

6. INVENTORS, WINESSES, AND DATE

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Inventor _____ Date_____

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READ AND UNDERSTOOD BY:

Witness: _____ Date_____

Witness: _____ Date_____

Witness: _____ Date_____

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